

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 January 2002 (31.01.2002)

PCT

(10) International Publication Number
WO 02/08821 A1

(51) International Patent Classification⁷: **G02F 1/00**,
G02B 5/23

(21) International Application Number: PCT/IL01/00552

(22) International Filing Date: 17 June 2001 (17.06.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/217,708 12 July 2000 (12.07.2000) US

(71) Applicant (for all designated States except US): **SKYRAD LTD.** [IL/IL]; Gutwirin Science Park, Technion, 32000 Haifa (IL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **FARAN, Ori** [IL/IL]; Beilis Street 4/6, 34814 Haifa (IL). **NATAN, Ezra** [IL/IL]; Alexander Yannay Street 46/2, 34816 Haifa (IL).

(74) Agent: **AGRANOV, David**; Moriah Ave. 20, 34571 Haifa (IL).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- with amended claims and statement

Date of publication of the amended claims and statement:

23 May 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: THERMOCHROMIC COMPOSITION

(57) **Abstract:** A novel reversible thermochromic composition comprising (1) a main organic component, capable to change its color upon applying thermal energy thereto and (2) an auxiliary organic component, rendering said main organic component the capability to change its color at predetermined temperature. Both components are incorporated within a polymer matrix. The articles made of this composition change their color or became colorless at predetermined temperature and they have accurate temperature response. The manufacturing process is simple, inexpensive and can be carried out by conventional technology routes.



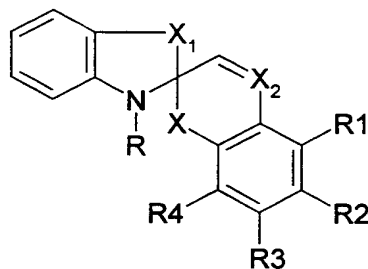
WO 02/08821 A1

AMENDED CLAIMS

[received by the International Bureau on 10 February 2002 (10.02.02);
original claims 1-7 replaced by amended claims 1-6 (4 pages)]

1. A thermochromic composition comprising
- 5 a) at least one chromogenic organic component, capable to change the color of the composition or discolorate thereof upon applying thermal energy,
- b) at least one stabilizing organic component, capable to render the change of color or discoloration visually detectable
- wherein said chromogenic organic component is selected from the group comprising:
- 10

- i) Spirobenzopyrans derivatives, having general formula A



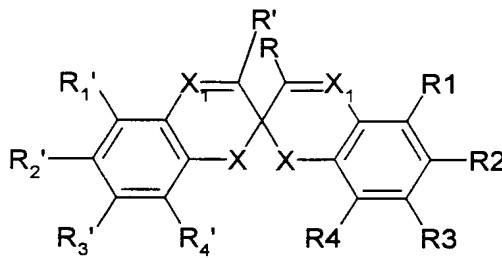
A

in the above formula $X = O$ or S ; $X_1 = O, S$ or $CR'R''$ where R' and R'' are independently a hydrogen, an alkyl group a halogen or only a sole group. like a substituted alkyl ring; $X_2 = N$ or CH ; and R, R_1, R_2, R_3, R_4 , represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. $R_1-R_2, R_2-R_3, R_3-R_4$ can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

15

20

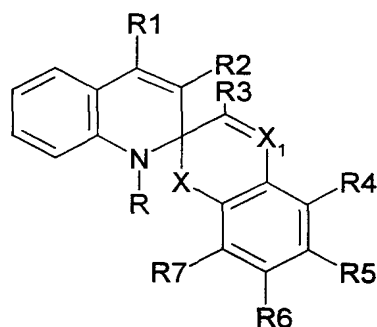
- ii) Spiropyranopyrans derivatives, having general formula B



B

in the above formula $X = O$ or S ; $X_1 = N$ or CR_5 ; and $R, R_1, R_2, R_3, R_4, R_5, R', R_1', R_2', R_3', R_4'$ represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. $R_1-R_2, R_2-R_3, R_3-R_4, R_1'-R_2', R_2'-R_3', R_3'-R_4'$ can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

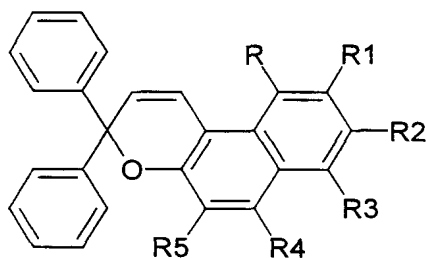
iii) Spiroquinolinopyrans derivatives, having general formula C,



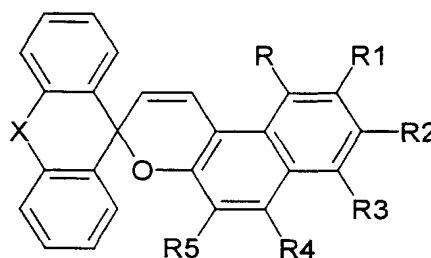
C

in the above formula $X=O$ or S ; $X_1=N$ or CR' ; and $R', R, R_1, R_2, R_3, R_4, R_5, R_6, R_7$ represent independently a hydrogen, an alkyl group, a functionalized group, an alkoxy group, a nitro group or a halogen. $R_4-R_5, R_5-R_6, R_6-R_7$ can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

iv) Naphthopyrans derivatives, having general formula D or E



D



E

in the above formulae $X=O, S, N-R'$ with R' an alkyl group or a functionalized group, $(CH_2)_n$ and $n=0, 1$. $R, R_1, R_2, R_3, R_4, R_5$ represent independently a hydrogen an alkyl group, a functionalized group, an alkoxy

group, a nitro group or a halogen. R-R₁, R₁-R₂, R₂-R₃, R₄-R₅ can also represent independently only a sole group, like a substituted alkyl ring or a substituted aromatic group,

and said stabilizing organic component is selected from the group comprising

- 5 - Benzylidene-1,1'-di-2-naphthol
- 2-hydroxybenzylidene-1,1'-di-2-naphthol
- 3-hydroxybenzylidene-1,1'-di-2-naphthol
- 3-aminobenzylidene-1,1'-di-2-naphthol
- 3-nitrobenzylidene-1,1'-di-2-naphthol
- 10 - 3-hydroxybenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-aminobenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-nitrobenzylidene-1,1'-di-2-naphthol
- 2-hydroxy-3-methoxybenzylidene-1,1'-di-2-naphthol
- 2-chloro-5-nitrobenzylidene-1,1'-di-2-naphthol
- 15 - 2-chloro-5-aminobenzylidene-1,1'-di-2-naphthol
- 3-amino-4-hydroxy-5-methoxybenzylidene-1,1'-di-2-naphthol
- 4,4'-isopropylidenediphenol
- 4,4'-isopropylidenebis(2,6-dimethyl-phenol).
- 4,4'-ethylidenebisphenol
- 20 - Bis(4-hydroxyphenyl)methane
- Bis(4-glycidyloxyphenyl)methane
- 4,4'-(1,3-phenylenediisopropylidene)bisphenol
- 4,4'-sulfonyldiphenol
- 4,4'-cyclohexylidenebisphenol
- 25 - 4,4'-isopropylidenediphenol
- 4,4'-isopropylidenebis(2,6-dimethyl-phenol)
- 4,4'-ethylidenebisphenol
- Bis(4-hydroxyphenyl)methane
- Bis(4-glycidyloxyphenyl)methane
- 30 - 4,4'-(1,3-phenylenediisopropylidene)bisphenol
- 4,4'-sulfonyldiphenol
- 4,4'-cyclohexylidenebisphenol
- α , α' -di(2-hydroxy-1-naphthyl)-p-tolyl-benzoic acid ester

- (α , α' -di(2-hydroxy-1-naphthyl)-o-tolyl)-sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphthalene

- (3-methoxy- α , α' -di(2-hydroxy-1-naphthyl)-p-tolyl)-sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphthalene

5 - { α -[2-(2-diazo-1,2-dihydro-1-oxo-5-naphthyl-sulphonyloxy)-1-naphthyl]- α -(2-hydroxy-1-naphthyl)-o-tolyl} sulphonic acid ester of 6-diazo-5,6dihydro-5-oxo-1-naphthalene

- Bis(2-methyl-3-indolyl)-methyl-p-anisol.

10 2. The thermochromic composition as defined in claim 1, in which said chromogenic component and said stabilizing component are incorporated within a polymeric matrix.

3. The thermochromic composition as defined in claim 2, said composition containing 0.005-0.5 % by weight of the chromogenic component, 0.05-2% by weight of the stabilizing component and the rest is polymeric matrix.

15 4. The thermochromic composition as defined in claim 3, in which said composition contains at least one functional additive, e.g. dye, pigment, UV absorber, antioxidant, reduction preventing agent, reducing agent, flame retardant, chelating agent etc.

20 5. The thermochromic composition as defined in claim 4, in which the amount of said functional additive is at least 0.1 % by weight.

6. The thermochromic composition as defined in claim 2, in which said polymeric matrix is selected from the group comprising polycarbonates, polystyrenes, polyolefins, polyacrylates such as polymethylmethacrylates, polyvinyl derivatives, polyester derivatives, polyvinyl chloride; cellulose derivatives such as cellulose acetate, polyurethanes, polyethylene terephthalate; silicone resins such as LSR (liquid silicone rubber), triethylene glycole dimethacrylate (TEGDM, commercially known as CR-39), epoxy resins.

30

STATEMENT UNDER PCT ARTICLE 19

Claim 1 (the main claim) of the above application has been amended to include combination of the following features:

- a) Presence of at least one chromogenic organic component
- b) Presence of at least one stabilizing organic component
- c) Specific chemical compounds for selecting chromogenic component, said compounds comprise spirobenzopyrasn derivates having formula A, B and C, naphtopyrans derivatives having formula D and E
- d) Specific compounds for selecting stabilizing organic component, said compounds are listed in originally filed claim 2.

The introduced amendments do not go beyond the disclosure in the above referred-to application as filed, they do not introduce any new matter and there is no impact on the description and the drawings.

In short the differences between the claimed invention and the cited references are as follows:

- a) In the cited references there is no mentioning of combination of chromogenic component with a stabilizing component and there is no mentioning of compounds for selecting chromogenic component and stabilizing component as in the present invention
- b) Concentration of chromogenic component employed in Byker reference is at least an order of magnitude higher than in the present invention
- c) Stabilizing component is not present in Byker reference at all.

Thus the Applicant respectfully requests reconsideration of the characterization of the cited references during Chapter II examination.